Acta Chemica Scandinavica A 31 (1977) 611—614

Jahn-Teller Distortions in the Structure of Manganese(III) Selenite Trihydrate, $Mn_2(SeO_3)_3.3H_2O$

MARKUS KOSKENLINNA and JUSSI VALKONEN

Department of Chemistry, Helsinki University of Technology, Otaniemi, SF-02150 Espoo 15, Finland

The crystal structure of manganese(III) selenite trihydrate, $Mn_2(SeO_3)_3.3H_2O$, has been determined by X-ray methods. The compound is monoclinic, and belongs to the space group $P2_1/c$ (No. 14) with $Z=4$. The crystal axes are $a=7.751(3)$ Å, $b=10.330(4)$ Å and $c=13.429(7)$ Å and the angle $\beta=92.74(3)°$. The structure was solved by direct methods and refined to $R=0.043$.

The three non-equivalent manganese atoms are octahedrally coordinated, and the coordination polyhedra exhibit Jahn-Teller distortions. All the octahedra are tetragonally elongated, and two of the three non-equivalent octahedra have an additional small axial distortion in the equatorial plane. Each selenium atom bridges three different MnO_6-octahedra, linking them into a three-dimensional network. The bonding scheme of the selenium is pyramidal and the bond lengths and angles are within the normal ranges.

In our earlier studies on divalent manganese selenites we described the relatively small and irregular distortions of the MnO_6-octahedra within the compounds $MnSeO_3.D_2O$ and $MnSeO_3.2H_2O$.[1,2] In divalent manganese ion the d-electron density is spherically distributed and does not contribute to the possible distortions of the coordination polyhedra. As a result, the MnO_6 octahedron may be quite regular in some compounds as in $MnSe_2O_5$, where the differences in bond lengths are statistically insignificant.[3] In this respect divalent manganese greatly differs from trivalent manganese, which is expected to exhibit distortions of the Jahn-Teller type in octahedral coordination owing to its high-spin d^4-configuration.

In the light of these studies it was considered interesting to see the effect of Jahn-Teller forces on the structure of manganese selenites. We therefore sought to prepare crystals of the selenite compounds of trivalent manganese. In this communication we describe the preparation and crystal structure of manganese (III) selenite trihydrate, $Mn_2(SeO_3)_3.3H_2O$.

EXPERIMENTAL

The compound was crystallized from a suspension of freshly precipitated hydrated manganese dioxide and concentrated selenous acid. 1.0 mol/dm³ selenous acid was added upon the manganese dioxide in the molar ratio 4:1 and the suspension was placed in a steel reactor with Teflon lining. The temperature was maintained at 100 – 140 °C for 2 – 4 days. Under these conditions, well-developed, lustrous, dark-brown prisms of $Mn_2(SeO_3)_3.3H_2O$ were grown. In the preparations, reagents of analytical grade were used.

The X-ray intensity data were recorded on a Syntex $P2_1$ (fortran-version) automatic diffractometer with graphite monochromatized Mo$K\alpha$-radiation. Reflections with 2θ values between 5 and 60° were recorded using the $\theta-2\theta$ scan technique and a scan speed of 1°/min. The unit cell was determined by measuring the positional parameters of 17 independent reflections with the diffractometer and the cell dimensions refined by the method of least-squares. The unit cell was monoclinic with dimensions $a=7.751(3)$ Å, $b=10.330(4)$ Å, $c=13.429(7)$ Å and $\beta=92.74(3)°$. The systematic absences in the original intensity data indicated the space group $P2_1/c$ (No. 14). There were four formula units in the unit cell. The calculated and measured (flotation) densities were 3.37 and 3.4 g cm^{-3}, respectively. With the criterion $I>4\sigma(I)$ a total of 1839 independent reflections were obtained and used in the subsequent calculations. Lorentz and polarization corrections were applied and the empirical absorption correction ($\mu=123.9$ cm^{-1}) was made on the basis of the ϕ-scan data.

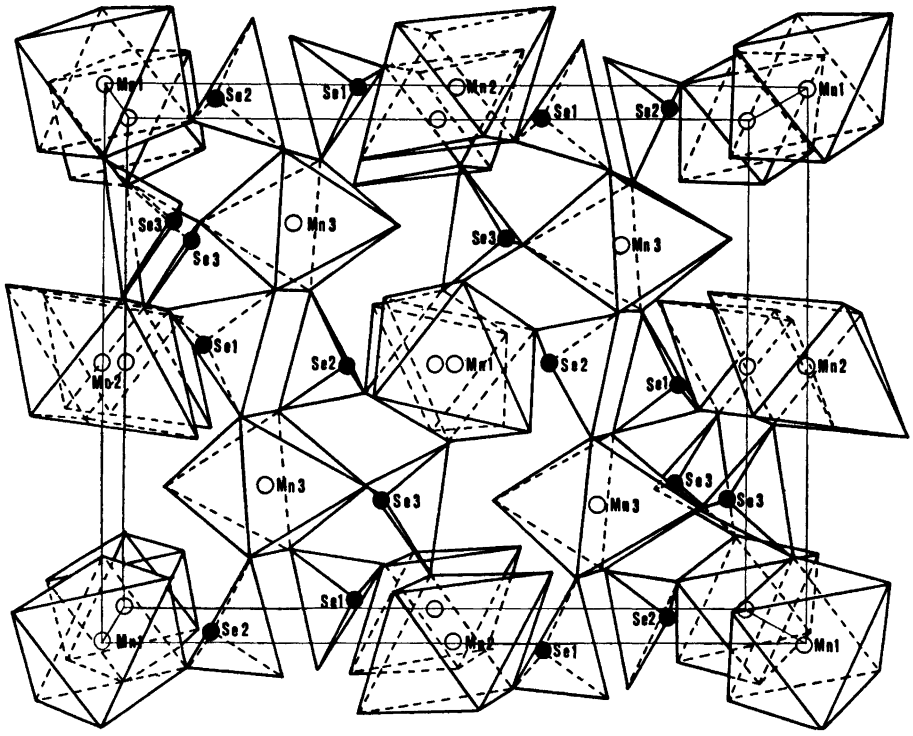

Fig. 1. Perspective view of the unit cell packing of $Mn_2(SeO_3)_3.3H_2O$ along the *b*-axis.

Table 1. Final positional and thermal parameters with their estimated standard deviations in parentheses. The anisotropic parameters are multiplied by 10^4; they are of the form: $\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})]$.

Atom	x	y	z	U_{11}	U_{12}	U_{33}	U_{12}	U_{13}	U_{23}
Mn1	0	0.5	0.5	111(11)	69(11)	141(12)	29(9)	−66(9)	−15(10)
Mn2	0	0.5	0	125(12)	63(11)	152(12)	18(9)	−55(10)	−25(10)
Mn3	.5405(2)	.7677(2)	.2700(1)	102(8)	36(7)	131(8)	−1(6)	−46(6)	−6(6)
Sel	.6498(1)	.0386(1)	.3642(1)	137(5)	69(5)	146(5)	0(4)	−41(4)	5(4)
Se2	.6691(1)	.4965(1)	.3515(1)	138(5)	75(5)	145(5)	7(4)	−40(4)	−3(4)
Se3	.1734(1)	.2490(1)	.3978(1)	130(5)	88(5)	138(5)	4(4)	−34(4)	1(4)
O1	.2856(11)	.3990(8)	.1950(7)	125(39)	89(37)	248(47)	−5(31)	−7(34)	74(34)
O2	.3674(11)	.6350(8)	.2413(6)	188(44)	139(40)	144(43)	−53(34)	−14(34)	−29(33)
O3	.1547(11)	.5949(8)	.0904(7)	191(44)	99(39)	270(51)	52(33)	−145(38)	−20(36)
O4	.6325(11)	.4027(8)	.2454(6)	173(42)	101(37)	135(41)	−18(32)	−31(33)	−9(32)
O5	.7191(11)	.6394(8)	.2935(7)	135(41)	75(37)	232(46)	−33(30)	−48(35)	25(33)
O6	.8722(12)	.4396(8)	.3814(7)	233(47)	106(40)	257(49)	117(34)	−141(39)	−71(35)
O7	.8137(11)	.6075(8)	.0328(7)	181(44)	155(42)	188(45)	9(35)	−38(36)	−78(35)
O8	.6112(10)	.7704(8)	.1179(6)	84(40)	190(43)	189(43)	53(33)	6(31)	20(35)
O9	.1512(12)	.3566(9)	.4937(7)	259(50)	187(44)	139(43)	83(37)	−45(37)	−93(35)
O10	1.9453(12)	.3669(9)	.1365(7)	214(47)	215(47)	253(51)	−64(38)	−16(39)	43(39)
O11	.4578(12)	.7623(10)	.4289(7)	210(45)	350(55)	180(45)	3(42)	−67(36)	34(42)
O12	.8407(13)	.1212(9)	.1000(8)	302(55)	203(49)	328(56)	17(42)	−16(46)	−50(42)

The structure was resolved and refined with the aid of the crystallographic computer program X-Ray 1976.[4] For the scattering factors neutral atoms were presumed and their values were taken from the International Tables.[5] The positions of the manganese and selenium atoms were obtained by direct methods from the E-map calculated with 343 E-values bigger than 1.4. After refinement of these the value of R was 27.3 %. The positions of all the oxygens were found in the corresponding difference-Fourier map. The structure was then refined with isotropic temperature factors to an R value of 6.7 %. With anisotropic temperature factors using block-diagonal refinement the value of R was reduced to 4.3 %. The F_o and F_c listing is available from the authors upon request.

DISCUSSION

Final atomic coordinates and anisotropic temperature factors are given in Table 1. The manganese atoms labelled Mn(1) and Mn(2) are in two-fold special positions. The oxygen atoms O(1) – O(9) are all bonded to one of the three selenium atoms and O(10) – O(12) are due to water of crystallization. Selected bond distances and angles are given in Table 2.

The three non-equivalent manganese atoms are octahedrally coordinated by oxygens. The coordination polyhedra are in each case strongly distorted. Since the Mn – O bond lengths fall roughly into two classes, comprising four short and two longer distances, the distortion is mainly tetragonal elongation. Around Mn(1) and Mn(2) there are three pairs of identical Mn – O bonds on opposite sides of the manganese atoms and, as a further consequence of the two manganese atoms being in special positions, the angle O – Mn – O for each of these pairs is exactly 180°. The bond lengths

Table 2. Selected interatomic distances (Å) and bond angles (°) and their estimated standard deviations.

2 × Mn1 – O6	1.938(9)^{i,ii}		Se1 – O1	1.728(8)^{iii}	
2 × Mn1 – O9	1.893(9)^{i,ii}		Se1 – O2	1.731(9)^{iii}	
2 × Mn1 – O12	2.248(10)^{iii,iv}		Se1 – O3	1.708(9)^{iii}	
2 × Mn2 – O3	1.932(9)^{i,ii}		Se2 – O4	1.735(8)^{i}	
2 × Mn2 – O7	1.891(9)^{i,ii}		Se2 – O5	1.721(8)^{i}	
2 × Mn2 – O10	2.346(10)^{i,ii}		Se2 – O6	1.710(9)^{i}	
Mn3 – O1	1.954(8)^{iii}		Se3 – O7	1.734(9)^{iii}	
Mn3 – O2	1.944(9)^{i}		Se3 – O8	1.707(8)^{iii}	
Mn3 – O4	1.939(8)^{iii}		Se3 – O9	1.717(9)^{i}	
Mn3 – O5	1.932(8)^{i}				
Mn3 – O8	2.140(9)^{i}		O1^{iii} – Se1 – O2^{iii}	96.9(4)	
Mn3 – O11	2.258(9)^{i}		O1^{iii} – Se1 – O3^{iii}	100.1(4)	
			O2^{iii} – Se1 – O3^{iii}	97.4(4)	
O6^{i} – Mn1 – O6^{ii}	180.0(4)				
O9^{i} – Mn1 – O9^{ii}	180.0(4)		O4^{i} – Se2 – O5^{i}	98.0(4)	
O12^{iii} – Mn1 – O12^{iv}	180.0(4)		O4^{i} – Se2 – O6^{i}	96.5(4)	
O6^{i} – Mn1 – O9^{i}	90.3(4)		O5^{i} – Se2 – O6^{i}	100.1(4)	
O6^{i} – Mn1 – O12^{iv}	92.2(4)				
O9^{i} – Mn1 – O12^{iv}	87.1(4)		O7^{iii} – Se3 – O8^{iii}	98.3(4)	
			O7^{iii} – Se3 – O9^{i}	98.5(4)	
O3^{i} – Mn2 – O3^{ii}	180.0(4)		O8^{iii} – Se3 – O9^{i}	98.2(4)	
O7^{i} – Mn2 – O7^{ii}	180.0(4)				
O10^{i} – Mn2 – O10^{ii}	180.0(4)		O1^{iii} – Mn3 – O2^{i}	177.3(4)	
O3^{i} – Mn2 – O7^{ii}	89.2(4)		O4^{iii} – Mn3 – O5^{i}	176.1(4)	
O3^{i} – Mn2 – O10^{i}	86.3(4)		O8^{i} – Mn3 – O11^{i}	178.2(3)	
O7^{i} – Mn2 – O10^{ii}	90.4(4)		O1^{iii} – Mn3 – O11^{i}	90.6(4)	
			O2^{i} – Mn3 – O5^{i}	91.8(4)	
			O4^{iii} – Mn3 – O8^{i}	95.5(3)	

The superscripts denote the symmetry operations:

i x,y,z
ii $\bar{x},\bar{y},\bar{z}$
iii $\bar{x},1/2+y,1/2-z$
iv $x,1/2-y,1/2+z$

of the two Mn – O bond pairs in the equatorial planes of the two octahedra are almost equal; they differ by only 0.045 Å and 0.042 Å, a distance, which must be considered statistically significant ($>4\sigma$ in both cases), however.

The mean length of the four shorter Mn(3) – O bonds is 1.942 Å. Since the difference between the extreme values of the four shorter bonds is less than 3σ, the differences between these bonds are statistically insignificant. The two axial bond lengths differ markedly from each other. The reason for this is probably that the oxygen O(11) farther from Mn(3) is contributed by a water molecule, while O(8), the other axially bonded oxygen belongs to a selenite group.

It can be concluded that the distortion of the coordination polyhedra is mainly tetragonal, but in the case of Mn(1) and Mn(2) there is a further, distinctly smaller axial distortion in the equatorial plane. Thus, it appears that the coordination octahedra around Mn(1) and Mn(2) are orthorhombically distorted. An orthorhombically distorted MnO_6-octahedron has recently been detected in tris(tropolonato)-manganese(III), $Mn(O_2C_7H_5)_3$, in which one of the two nonequivalent MnO_6-octahedra had three pairs of bond lengths, and their weighted means were 2.051(16), 1.990(5) and 1.944(8) Å.[6]

The MnO_6-octahedra are considerably elongated as can be seen by comparing to some other Mn(III) compounds. In $Mn(O_2C_7H_5)_3$ the range of Mn – O bonds is 1.925(10) – 2.110(10) Å and in tris(2,4-pentanedionato)manganese-(III), $Mn(O_2C_5H_7)_3$, the range is from 1.931(10) to 2.020(7) Å.[7] In anhydrous manganic acetate, $Mn_3O(OAc)_6 \cdot AcOH \cdot OAc$, a compound of trivalent manganese containing also a distorted MnO_6-octahedron, the range is 1.85(4) – 2.24(4) Å.[8]

It must be emphasized, however, that it is difficult to estimate how large a portion of the distortion is due to the Jahn-Teller forces, since the hydrogen bonds have an effect on the distortion, too. In both $Mn(1)O_6$ and $Mn(2)O_6$ the two cap oxygens of the octahedron are contributed by water molecules, and the longest of the Mn – O bonds in $Mn(3)O_6$ which is formed with the oxygen of a water molecule, is of the same magnitude as the long bonds in $Mn(1)_6$ and $Mn(2)O_6$. The oxygen (O8) of the other long bond belongs to the selenite group, and the bond length is noticeably shorter. It is only slightly larger than the corresponding bonds in $Mn(O_2C_7H_5)_3$ and $Mn(O_2C_5H_7)_3$.

The bonds in the selenite groups are slightly longer than those in manganese(II) selenites.[1–3] The mean of the bond angles is also somewhat smaller. All the three nonequivalent selenite groups act as bridging ligands between three manganese atoms.

REFERENCES

1. Koskenlinna, M. and Valkonen, *Acta Chem. Scand. A 31* (1977). *In press.*
2. Koskenlinna, M., Niinistö, L. and Valkonen, J. *Cryst. Struct. Commun. 5* (1976) 663.
3. Koskenlinna, M., Niinistö, L. and Valkonen, J. *Acta Chem. Scand. A 30* (1976) 836.
4. The X-Ray System, Version of 1976, Stewart, J. M., Ed., *Technical Report TR-446 of the Computer Science Center*, University of Maryland, College Park, Maryland.
5. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. 4, p. 72.
6. Avdeef, A., Costamagna, J. and Fachler, J. P. *Inorg. Chem. 13* (1974) 1854.
7. Fachler, J. P. and Avdeef, A. *Inorg. Chem. 13* (1974) 1864.
8. Hessel, L. W. and Romers, C. *Recl. Trav. Chim. Pays-Bas 88* (1969) 545.

Received April 19, 1977.